mixing with a vortex mixer at 0.060 mg/mL (tomato), 0.070 mg/mL (peach). and 0.065 mg/mL (citrus).

Gradient Elution Moving Boundary Electrophoresis Device.

Reservoirs for the sample buffer and the run buffer were machined from polyoxymethylene and polysulfone, respectively. A 5.5 cm long fused silica capillary (Polymicro Technologies, Phoenix, Ariz.) with an outer diameter of ~363.5 μm and an inner diameter of ~13.5 μm was inserted through holes drilled into the sides of the reservoirs such that the capillary protruded ~1 mm into the sample reservoir and ~5 mm into the run buffer reservoir. Double-sided adhesive tape was affixed between the run buffer reservoir and the high pressure fitting (Upchurch, Vernon Hills, Ill.) to hold the capillary securely in place.

For analyte detection, the capillary was threaded through a TraceDec® contactless conductivity detector. The detection point was ~15 mm from the capillary inlet end into the sample reservoir. Detector settings were the following: frequency, 2× high; voltage, 0 dB; gain, 200%; offset, 14; filter, slow; and data acquisition rate, 19.8 Hz. Constant DC voltage (PS350, Stanford Research Systems) was applied during experiments via high purity platinum wires inserted into the reservoirs. A precision pressure controller (Series 600, Mensor, San Marcos, Tex.), backed by pressurized helium, controlled the pressure inside the sealed run buffer reservoir. Data were recorded using vendor supplied detector software (TraceDec® Monitor 0.07a). Custom LabView software controlled and monitored the pressure controller and high voltage source. The loosely sealed sample reservoir was at ambient pressure. The apparatus was contained inside an enclosure to minimize the effects of temperature fluctuations due to stray air currents on the detector signal.

Separation of Complex Samples.

A new capillary was filled by driving run buffer from the run buffer reservoir through the capillary using pressure. As soon as a bead of fluid was visible on the opposite end of the capillary inserted into the sample reservoir, the sample reservoir was filled with sample buffer. Before initial use, run buffer was flushed through the capillary for several minutes to form a coating of DDAB on the capillary surface. Prior to analysis of a new type of sample, the sample reservoir was rinsed three times with 18 MΩ cm water, rinsed once with the new sample solution, and filled with 200 μL of fresh sample solution for analysis. The sample was replaced between replicate separations. Analyte step/peaks were identified by performing separations of samples comprised of individual analytes prepared in sample buffer. Analysis of blank sample buffer after each sample indicated that contamination of the system by samples was below the limit of detection (LOD) of the apparatus. The apparatus was stored by replacing the fluid in the sample reservoir with 18 MΩ cm water and reducing the pressure to between 2 and 5 kPa.

Separation was effected by holding the pressure on the run buffer reservoir at a high constant pressure between 25 and 60 kPa for ~6 s. The high voltage was switched on, while the pressure was reduced to the starting pressure for that separation, and held for ~10 s. The pressure was subsequently decreased by 100 Pa/s until enough time had elapsed to allow the analytes of interest to elute through the capillary. The capillary was then flushed at high pressure, typically ~5 kPa larger than the pressure applied at the start of the separation, for at least ~10 s. The high voltage was switched off, and the system was held in this configuration for at least ~1 min before the start of the next separation.

DDAB served to reverse EOF in the capillary, so that the EOF opposed the electrophoretic motion of the cations analyzed. In this experiment, DDAB was reported to be unstable over a period of days, as evidenced by a slow shift of analyte elution to higher pressure as EOF in the capillary tended to zero. Rinsing the capillary with 0.1 mol/L sodium hydroxide and recoating with DDAB was therefore necessary once over the course of these experiments.

Data Analysis.

A summary of results obtained for cationic analytes measured in complex samples using GEMBE with contactless conductivity detection is set forth in Table I below.

TABLE I

	K	Ca	Na	Mg	Li
Sample Buffer					
LOD (μmol/L)	0.22	0.31	0.67	0.27	0.39
RSD[a] (%)	0.45	0.49	2.40	0.71	0.44
Milk (Diluted 1000×)					
C (μmol/L)	44.7 ± 0.9	32.1 ± 0.9	21.1 ± 0.4	5.9 ± 0.4	
recovery[b] (%)	99 ± 2	109 ± 3	106 ± 2	91 ± 2	
RSD[a] (%)	0.85	0.64	0.86	1.39	
Dirt (5.0 mg/mL)					
C (μmol/L)	13.8 ± 0.7	142 ± 65 (811 ± 2.7)[d]	7.1 ± 0.8	18.8 ± 1.5	
recovery[b] (%)	100 ± 4.3	58 ± 27	93 ± 6	84 ± 6	
RSD[a] (%)	0.90	1.61	3.32	1.55	
Estuarine Sediment (0.28 mg/mL)					
C (μmol/L)	3.6 ± 0.3	20.6 ± 1.3	54.4 ± 0.9	10.3 ± 1.0	
recovery[b] (%)	5.8 ± 0.8	56.8 ± 7.1	60.3 ± 6.3	23.0 ± 3.3	
RSD[a] (%)	8.07	5.65	1.43	8.71	
Coal Fly Ash (18.8 mg/mL for K, 0.095 mg/mL for Ca, Na, Mg)					
C (μmol/L)	26.4 ± 0.5	49.4 ± 0.7	9.8 ± 1.1	12.3 ± 0.9	
recovery[b] (%)	0.28 ± 0.01	138.1 ± 63	118.0 ± 13.6	65.3 ± 5.1	
RSD[a] (%)	188	0.16	9.99	5.51	
Tomato Leaves (0.060 mg/mL)					
C (μmol/L)	41.4 ± 0.2	60.3 ± 1.0	1.0 ± 0.6	22.7 ± 0.7	
recovery[b] (%)	99.9 ± 10.2	79.8 ± 8.2	282 ± 172	76.6 ± 8.6	
RSD[a] (%)	0.08	1.13	39.3	1.25	